A Potential Distribution Induced Mapping of Free Energies for Nonuniform Simple Fluids

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The potential distribution theorem (PDT) is utilized to construct an effective density, the *pseudo-density* $\rho_{pseudo}(z)$, that enables mapping of the free energies of the uniform fluid exactly onto the nonuniform system values. In addition, a similar quantity, the *pseudo-chemical potential* $\mu_{pseudo}(z)$, is given as the chemical potential produced by the uniform equation of state upon using the nonuniform density $\rho_w^{(1)}(z)$ as input. The PDT connects three quantities: the work $W_{ins}(z)$ for inserting a test particle into the fluid, the chemical potential μ_0 of the bulk fluid, and the nonuniform singlet density $\rho_w^{(1)}(z)$. We perform Metropolis NVT ensemble Monte Carlo (MC) simulations to obtain the insertion work $W_{ins}(z)$ (via Widom's particle insertion) and the densities $\rho_w^{(1)}(z)$. We illustrate the mapping on two simple fluids adsorbed on a hard wall: the Lennard-Jones and the attractive Yukawa fluids. We characterize the behavior of the effective density and the pseudo-chemical potential vis-à-vis the cases of enhancement and depletion of the fluid density near the wall. These quantities (ρ_{pseudo} & μ_{pseudo}) are found to exhibit for enhanced adsorption out-of-phase oscillations compared to $\rho_w^{(1)}(z)$ and $\beta W_{ins}(z)$. For depleted adsorption, we do not observe oscillations and the trends of ρ_{pseudo} and μ_{pseudo} are in good agreement with those of $\rho_w^{(1)}(z)$ and βW_{ins}. We analyze the differences in behavior in terms of the concavity of the chemical-potential function.